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PENTAFLUOROPHENYL DERIVATIVES OF TRICOVALENT ALUMINIUM

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We report the preparation of the first fluorocarbon derivatives of tricovalent aluminium, pentafluorophenylaluminium dibromide, and bis(pentafluorophenyl)aluminium bromide. Complexes in which aluminium is coordinatively saturated, and containing perfluoroalkyl,[1] perfluorovinyl,[2] or, more recently, pentafluorophenyl groups[3] e.g. $LiAl(C_3F_7)_2I_2$, $Me_3N{\cdot}Al(CF{=}CF_2)_3$, and $LiAl(C_6F_5)_2Br_2$ respectively, have been reported and tris(pentafluorophenyl)aluminium etherate, $(C_6F_5)_3Al{\cdot}Et_2O$, has been prepared recently but attempts to obtain the tricovalent compound, i.e. free of ether, were unsuccessful even using the reaction between bis(pentafluorophenyl)mercury and aluminium.[4,5] Perfluoroalkyl or perfluorovinyl derivatives of tricovalent aluminium have not been characterised and are probably unstable due to migration of fluorine from carbon to aluminium, by analogy with the known instability of the corresponding boron compounds.[6]

The use of methylpentafluorophenylmercury in the preparation of pentafluorophenyltin halides has already been reported[7] and we now find that reaction of methylpentafluorophenylmercury with an exactly equivalent amount of aluminium tribromide gave pentafluorophenylaluminium dibromide quantitatively and methylmercury(II)bromide which was insoluble in petroleum ether.

$$MeHgC_6F_5 + AlBr_3 \xrightarrow[\text{Ether}]{\text{Petroleum}} MeHgBr + C_6F_5AlBr_2$$

Filtration and then removal of solvent under high vacuum for a long period left pentafluorophenylaluminium dibromide as a liquid. Similarly, pentafluorophenylaluminium dibromide with a further equivalent quantity of methylpentafluorophenylmercury gave bis(pentafluorophenyl)aluminium bromide.

$$MeHgC_6F_5 + C_6F_5AlBr_2 \xrightarrow[\text{Ether}]{\text{Petroleum}} MeHgBr + (C_6F_5)_2AlBr$$

The products were characterised by halogen analysis and in the former case by cleavage of pentafluorophenyl. Understandably, pentafluorophenylaluminium halides are exceedingly sensitive to oxygen and moisture and are hydrolysed with explosive violence. However, a sample of pentafluorophenylaluminium dibromide heated in a Carius tube, sealed under vacuum, did not decompose until 180° whereupon carbon was produced. This relative thermal stability of pentafluorophenylaluminium compounds is probably associated with partial co-ordinative saturation of aluminium by p-π bonding with pentafluorophenyl since evidence has been advanced for a similar stabilisation of pentafluorophenylboron compounds.[8]

Cleavage of methylpentafluorophenylmercury with other halides has been achieved; arsenic- and phosphorus-tribromides give the corresponding pentafluorophenylarsenic- and pentafluorophenylphosphorus-dibromides but difficulties are encountered in isolating these compounds pure since methylmercury(II)bromide appears to be partly soluble in the products. Reaction of methylpentafluorophenylmercury with germanium tetrabromide gave pentafluorophenyltribromogermane.

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